# STRUCTURE STUDIES ON HIGH AND LOW TEMPERATURE BUTADIENE POLYMERS AND COPOLYMERS

BY

DONALD JAMES SHIELDS

B.S., Lafayette College, 1944

## AN ABSTRACT OF A THESIS

SUBMITTED IN PARTIAL FULFILLMENT OF THE REQUIREMENTS
FOR THE DEGREE OF DOCTOR OF PHILOSOPHY IN CHEMISTRY
IN THE GRADUATE COLLEGE OF THE
UNIVERSITY OF ILLINOIS, 1949

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# STRUCTURE STUDIES ON HIGH AND LOW TEMPERATURE BUTADIENE POLYMERS AND COPOLYMERS

## Introduction

Recently, several investigators have discovered that butadiene-styrene copolymers (GR-S) polymerized at low temperatures can be fabricated into tires which have properties superior to those made from similar high-temperature synthetic rubbers. However, no chemical evidence has as yet been published which explains this superiority. The present work was undertaken in order to discover, by examination of their degradation products, differences (if any) between the skeletal structures of polymers (polybutadienes) made at different temperatures. In the course of the investigation, an attempt to improve reported recipes for the preparation of — 20° C polybutadiene was made, and an investigation of the mechanism of the formation of gelled polymers was undertaken.

## Discussion Of Results

I. *Preparation of Low Temperature GR-S:* A redox polymerization recipe which contained no modifier but which gave high-viscosity, soluble polymers in 36 hours at — 20° C was devised. The system, however, did not give reproducible results and yielded low-molecular weight polymers almost as often as it did good ones. Investigation revealed that careful elimination of air (oxygen) from the redox activator components of the system both during and after their combination, was a necessary and sufficient condition for obtaining reproducible results with the recipe used. Large-scale runs, charged under nitrogen, were reproducible and yielded polymers with very high (between four and five) intrinsic viscosities.

II. *The Structure of High and Low Temperature Polybutadienes:* Polybutadienes prepared at different tempera-

tures, on ozonization and treatment of the resultant ozonides with dilute hydrogen peroxide, yielded mixtures of carboxylic acids. The acids from each of the four polymers examined were separated by the newly-developed method of partition chromatography, and those more polar than succinic acid isolated and identified.

Two of the polybutadienes examined had been prepared at — 18° C and 5° C respectively; both were soluble. The other two had been polymerized at 50° C: One of them contained a modifier and was soluble; the other contained no modifier and was gelled and insoluble. The acids obtained from the — 18° C, 5° C, and modified 50° C polybutadienes did not differ appreciably and indicated parent polymers whose skeletal structures were essentially linear and consisted of butadiene molecules joined together in a 1,4-manner with occasional single 1,2-butadiene units along the chain. The polymers probably differed in molecular weight, the low-temperature ones having longer chains. A very important difference, however, existed in the products from the gelled polybutadiene. This polymer gave rise to an additional acid — tricarballylic, a species which could be accounted for only if the following reactions were assumed to have taken place: (1) Free radical attack at a position allylic to a double bond between adjacent 1,4-units along an already-formed polymer chain; and (2) 1,4-addition of butadiene monomer to the resultant polymer free radical.

Previous authors have classified gelled polybutadiene as *cross-linked* polymer, claiming that branching through allylic hydrogens could not lead to the formation of gel. However, the presence of tricarballylic acid in the acids from gelled polybutadiene seemed to us to indicate that branching through allylic hydrogens was an important, if not the only, factor in the formation of gelled polymer. It was therefore considered possible that extensive branching, which proceeded via free radical attack at allylic positions on already-formed polymer chains, was responsible for the gelled portions of the polymer and that *cross-linking* as defined by Flory[1] may not have occurred.

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## VITA

The author was born in Providence, Rhode Island on November 12, 1923. He received his elementary education in the public schools of Lowell, Massachusetts and his secondary education at Mount Hermon Preparatory School, Mount Hermon, Massachusetts, from which he was graduated in 1940. He entered Lafayette College in September, 1940 and received the Bachelor of Science Degree in Chemistry in December, 1943. He was employed as a research chemist by Tennessee Eastman Corporation until December, 1944 at which time he entered the United States Navy. He was commissioned in September, 1945 and was returned to inactive duty in September, 1946. This same month he entered the Graduate School of the University of Illinois. Since February, 1947 he has held a special research assistantship on the Government Rubber Research Program.

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